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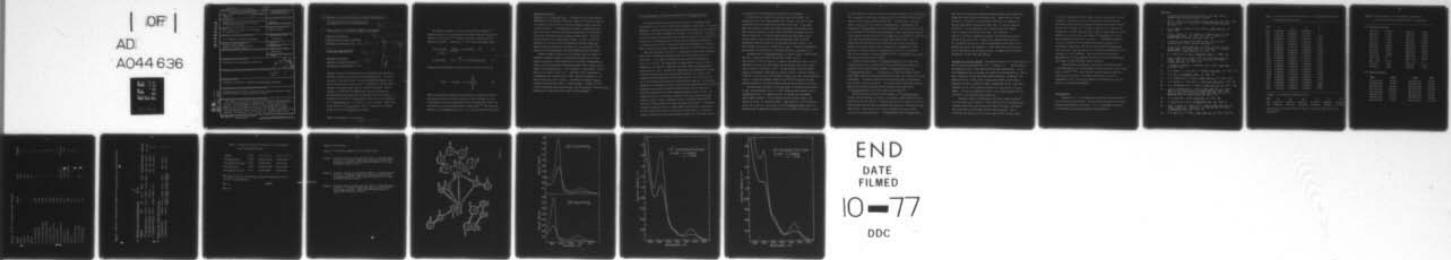
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The product resulting from reaction of photogenerated $(\eta^5-C_5H_5)_2W_2(CO)_4$ and C_2H_2 has been structurally characterized as having a tetrahedrane-like W_2C_2 core. The W-W distance is 2.973 Å in the $(\eta^5-C_5H_5)_2W_2(CO)_4(C_2H_2)$ complex and is ~0.25 Å shorter than in $(\eta^5-C_5H_5)_2W_2(CO)_6$ but is longer than that expected for the W-W triple bond. The C-C bond in the adduct is 1.35 Å or about 0.15 Å longer than in free C_2H_2. The near-uv absorption in the C_2H_2 adduct is assigned to a $\sigma_b \to \sigma^*$ absorption (λ_{max}=352nm; ϵ=6000 in C_6H_6).

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Synthesis and X-ray Crystallographic Structural Determination of the Acetylene Complex $(\eta^5-C_5H_5)_2W_2(CO)_4(C_2H_2)$.

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Summary: Reaction of photogenerated $(\eta^5-C_5H_5)_2W_2(CO)_4$ with acetylene at 25° yields a complex of the formula $(\eta^5-C_5H_5)_2W_2(CO)_4(C_2H_2)$. The crystal structure of the complex shows it to have a tetrahedrane-like W_2C_2 core. The C-C bond distance of the C_2H_2 unit is 1.35 $\overset{\circ}{A}$ which is close to that of ethylene, considerably longer than the 1.20 $\overset{\circ}{A}$ for acetylenes. The W-W distance is 2.973 $\overset{\circ}{A}$ which is ~0.25 $\overset{\circ}{A}$ shorter than the W-W distance in $(\eta^5-C_5H_5)_2W_2(CO)_6$ but longer than that expected for $(\eta^5-C_5H_5)_2W_2(CO)_4$. By analogy to the parent $(\eta^5-C_5H_5)_2M_2(CO)_6$ species, the near-uv absorption in $(\eta^5-C_5H_5)_2M_2(CO)_4(C_2H_2)$ is assigned to a $\sigma_b \rightarrow \sigma^*$ transition. Owing to the shorter M-M bond in the C_2H_2 adducts, the $\sigma_b \rightarrow \sigma^*$ absorption is at higher energy than in the $(\eta^5-C_5H_5)_2M_2(CO)_6$ complexes.

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The chemistry indicated in reaction (1) was recently reported.[2,3] Subsequent reaction of the metal-metal triple bonded complex with C_2H_2 occurs according to reaction (2).[2b,3] Reaction (2) seems to represent the only example of the direct reaction of a triple metal-metal bonded complex

$$(\eta^5\text{-}C_5H_5)_2M(CO)_6 \xrightarrow[h\nu\ @\ 25^\circ]{\Delta\ or} (\eta^5\text{-}C_5H_5)_2M(CO)_4 + 2CO \qquad (1)$$
$$M = Mo,\ W$$

$$(\eta^5\text{-}C_5H_5)M(CO)_4 + C_2H_2 \xrightarrow{25^\circ} (\eta^5\text{-}C_5H_5)_2M(CO)_4(C_2H_2) \qquad (2)$$
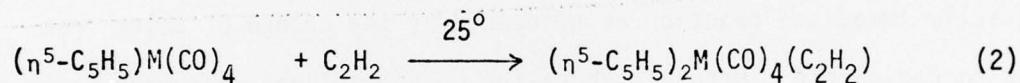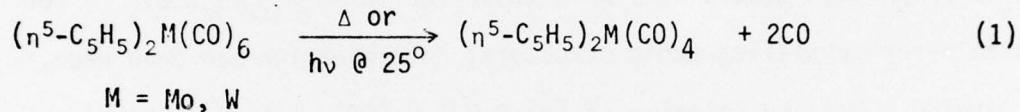
with another triple bonded species. The reaction may be viewed as in reaction (3).

$$M \equiv M + RC \equiv RC \longrightarrow \begin{array}{c} R \\ | \\ C \\ M \diagup\!\!\!\!\!\diagdown M \\ C \\ | \\ R \end{array} \qquad (3)$$
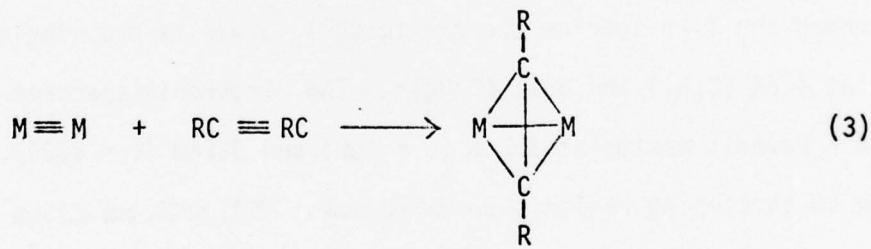
Owing to the potential importance of such reactions in building up clusters, and acetylene-containing clusters especially, we have undertaken an x-ray crystallographic structural determination of the acetylene adduct formed from the reaction of C_2H_2 and photogenerated $(\eta^5\text{-}C_5H_5)_2W_2(CO)_4$.[2b] Some structural features of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_2R_2)$ (R = C_2H_5, H) have already been reported.[4]

Results and Discussion

Synthesis of $(\eta^5\text{-}C_5H_5)_2W_2(CO)_4(C_2H_2)$. Irradiation of an Ar-purged benzene solution of $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ with near-uv light at $25°$ leads to the decline of ir bands at 1958 and 1910 cm^{-1} and the concomitant growth of new bands at 1885 and 1830 cm^{-1}. Accompanying these changes is a general decline of the near-uv and vis absorption spectrum associated with $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$. The original red-purple solution ultimately becomes yellow. The yellow solution contains the $(\eta^5\text{-}C_5H_5)_2W_2(CO)_4$ species. Its pmr, ir and uv-vis properties are in accord with this formulation,[2] and the synthesis and spectral properties accord well with those for $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$[2,3] for which an x-ray crystallographic structural determination has been made.[3]

Purging a benzene solution of $(\eta^5\text{-}C_5H_5)_2W_2(CO)_4$ with C_2H_2 results in essentially immediate reaction as evidenced by the change of color from yellow to red-purple. Rotary evaporation of the solvent, chromatography on alumina, and recrystallization from benzene-pentane yields a complex of the formula $(\eta^5\text{-}C_5H_5)_2W_2(CO)_4(C_2H_2)$. The C,H analysis is satisfactory: Calcd, C, 30.2; H, 1.9; found, C, 30.2; H, 2.1. Consistent with its formulation as a tetrahedrane-like species the pmr in $CDCl_3$ exhibits two singlets in a 5:1 ratio at 4.64 (C_5H_5) and 6.11 (C_2H_2)τ. The electronic spectrum in benzene at $298°K$ reveals maxima at 525 nm (ε = 900) and 352nm (ε = 6000), and the ir in the CO stretching region shows three peaks: 1990, 1922, and 1835cm^{-1} (isooctane solvent). These spectral properties parallel those for the Mo analogue.[3]

X-ray Crystallographic Structural Determination of $(\eta^5-C_5H_5)_2W_2(CO)_4(C_2H_2)$.

    The crystal used for data collection had the form of a rectangular plate with dimensions 0.35 x 0.30 x 0.20 mm, and was mounted on a glass fiber. Preliminary photographs indicated the monoclinic space group $P2_1/n$ with the unit cell dimensions a=10.257(4), b=17.146(5), c=8.582(3) Å, β=94.54(2)°, Z=4, V=1504.6 Å^3. The precise unit cell parameters were determined from the setting angles of 36 well-centered reflections on a diffractometer. Other relevant data are: molecular weight=635.8, calculated density=2.81g cm^{-3}, measured density=2.78g cm^{-3}(obtained via flotation from an aqueous ZnI_2 solution), absorption coefficient=161 cm^{-1}(for MoKα X-rays).

    Data were collected in the ($\pm$h, +k, -ℓ) quadrant on a Nonius CAD-3 diffracto-meter with Zr-filtered MoKα radiation by the θ/2θ scan technique up to a 2θ limit of 45°. A scan speed of 10°/minute was used with the scan defined as Δθ=(1.2 + 0.1 tan θ)°. Each reflection was scanned between two and six times, depending on its intensity. Background counts were taken at the beginning and at the end of each scan. Zirconium foil attentuators were automatically inserted to prevent the count rate from exceeding 2500 counts/sec. As a check on the stability of the diffractometer and the crystal, the (0, 12, 0), ($\bar{6}$, 0, 0) and (0, 0, $\bar{4}$) reflections were measured at fifty-reflection intervals. No significant variation in the intensities of these reflections was observed during data collection. Subsequent data processing reduced the 3576-reflection data set (containing 2431 unique reflections) into 1979 independent reflections with I > 3σ(I). The standard deviation of ecah intensity reading, $\sigma(F_o^2)$, was estimated using the expression $\sigma(F_o^2)$ = [(peak + background counts) + (0.04)^2(net intensity)^2]$^{1/2}$. Values of F_o^2 were corrected for Lorentz and polarization effects. An empirical absorption correction curve was applied based on the variation in intensity of an axial reflection (at χ=90°) as a function of spindle angle ϕ. Transmission factors (normalized to unity) varied between 0.53 and 1.29: this large variation

is consistent with the high absorption coefficient of the compound.

The structure was solved with conventional heavy atom methods: the coordinates of the W atoms were obtained from a Patterson map, and all other non-hydrogen atoms were located from difference Fourier maps. In the subsequent least-squares refinement, the thermal parameters of the tungsten atoms were refined anisotropically, while those of the carbon and oxygen atoms were refined isotropically. A final difference Fourier map showed some residual electron density in the vicinity of the cyclopentadiene rings, indicating considerable librational motion of the rings about the metal-ring axis. The final agreement factors are R = 0.063 and R_w = 0.069. A listing of the observed and calculated structure factors is available from one of the authors (R.B.).

An ORTEP plot of $(\eta^5-C_5H_5)_2W_2(CO)_4(C_2H_2)$ is shown in Figure 1, and the atomic positions, distances and angles are set out in Tables I and II. The W-W bond is 2.973(1) Å long and is bridged by the acetylene group in a nearly perpendicular fashion (the angle between the W-W bond and the C-C bond, looking down the center of both bonds, is 87°). The bond distances from the tungsten atoms to the acetylenic carbon atoms are identical within 3σ and their average is 2.15(2) Å. While this part of the molecule, the W_2C_2 core, looks quite symmetrical, there is a single semi-bridging carbonyl group [C(1)O(1)] that makes the whole molecule asymmetrical and the environments about the two W atoms quite different.

The data support formulation of the C_2H_2 adduct as one containing essentially an M_2C_2 pseudotetrahedral core, as in other dimetal-acetylene complexes such as $Co_2(CO)_6(C_2R_2)$.[6] Thus, the schematic reaction (3) between two triple-bonded species seems reasonable. The W-W distance and the C(5)-C(6) distance also support the notion of a saturated complex. Some reference C-C and M-M distances are set out in Table III. We see that in the $(\eta^5-C_5H_5)_2W_2(CO)_4(C_2H_2)$ complex the C(5)-C(6) bond is lengthened considerably from the 1.204 Å[5] in free C_2H_2 to a value

of 1.35(3) Å which is close to that for the C-C bond in ethylene. The bond lengthening is comparable to that found in $Co_2(CO)_6(C_2R_2)$[6] (R=Ph, tBu) and $(\eta^5-C_5H_5)_2Ni_2(C_2Ph_2)$[7] which also have the M_2C_2 tetrahedrane-like core. The W-W distance in the C_2H_2 adduct is shorter than in the parent $(\eta^5-C_5H_5)_2W_2(CO)_6$.[8] Unfortunately, the structure of $(\eta^5-C_5H_5)_2W_2(CO)_4$ has not been determined. But from the data for the Cr-Cr[9] and Mo-Mo[3] triple bonded species compared to their single bonded analogues,[8] we can estimate the W≡W distance in $(\eta^5-C_5H_5)_2W_2(CO)_4$ to be 2.45±0.01 Å, significantly less than that determined here for the C_2H_2 adduct [2.973(1) Å]. Thus, it appears that some saturation of the W≡W bond and the C≡C occurs upon adduct formation, but neither multiple bond is saturated to a representative single bond value. The Co-Co distance in $Co_2(CO)_6(C_2R_2)$[6] of ~2.47 Å is also shorter than the Co-Co distance in either $Co_2(CO)_8$ (2.52 Å)[10] or $Co_2(CO)_6(P(n-Bu)_3)_2$ (2.66Å).[11] These data parallel the present findings.

The most striking feature in $(\eta^5-C_5H_5)_2W_2(CO)_4(C_2H_2)$ is the single semi-bridging carbonyl group, a feature which has also been observed by Cotton and co-workers in the closely related compounds $(\eta^5-C_5H_5)_2Mo_2(CO)_4(C_2H_2)$ and $(\eta^5-C_5H_5)_2Mo_2(CO)_4(C_2Et_2)$.[4] The presence of a single semi-bridging carbonyl group (SBCO) between two otherwise equivalent metal atoms runs contrary to intuitive expectations. To preserve symmetry, one would normally expect a complementary pair of SBCO's, one from each metal. In a recent article, Cotton and co-workers have made the plausible argument that the presence of the single SBCO in $(\eta^5-C_5H_5)_2Mo_2(CO)_4(C_2H_2)$ can be attributed to steric effects.[4b]

The non-linearity of the W(1)-C(1)-O(1) angle in $(\eta^5-C_5H_5)_2W_2(CO)_4(C_2H_2)$ [167(2)°] and the closeness of the W(2)...C(1) contact distance [2.86(2) Å, much shorter than the other three W...C distances which are all in excess of 3.3 Å], are both consistent with the idea that incipient bond formation is taking place between W(2) and C(1). There appears to be a hint of something like this occurring also in the triple-bonded species $(\eta^5-C_5H_5)_2Mo_2(CO)_4$ and $(\eta^5-C_5Me_5)_2Cr_2(CO)_4$:

their very low CO stretching frequencies indicate unusually large interactions
between the carbonyl groups and the metal atoms. Indeed, the M'-M-C angles
and the M'···C distances in these molecules (Table IVb) are comparable to
those of semi-bridging carbonyl groups (Table IVa). It looks as though the
CO orbitals in $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$ and $(\eta^5\text{-}C_5Me_5)_2Cr_2(CO)_4$ are "bending
over" to interact with the M≡M triple bond. This interaction
could be in the form of enhanced back-donation from the electron density of
the M≡M triple bond to the π* orbitals of CO, combined perhaps with some
OC → M donation from the C = O π bond to an appropriately empty metal orbital.
Whatever the form of the interaction, it seems clear that the CO bond orders
in $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$ and $(\eta^5\text{-}C_5Me_5)_2Cr_2(CO)_4$, as judged by their stretching
frequencies, are lower than they should be.

Assignment of Electronic Spectrum. The electronic spectra of $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4(C_2H_2)$
and $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ (M=Mo,W) are shown in Figures 2 -4. The C_2H_2 adducts
are remarkably similar to each other as are the parent hexacarbonyls. For all
four compounds we find a low energy, low intensity visible absorption at ~500 nm,
and in the near-uv we find a much more intense transition. The energy of the
bands for M=W are a little higher in energy than for M=Mo, and the near-uv
transition for the C_2H_2 adducts is higher in energy than for the parent hexa-
carbonyls but the visible absorption maximum is at lower energy in the C_2H_2
adducts. The data are summarized in Table V, and a common assignment for the
absorption in the complexes appears appropriate.

The near-uv band in the hexacarbonyls has been assigned previously[12]
to a metal-metal $\sigma_b \to \sigma^*$ transition. The position of the $\sigma_b \to \sigma^*$ absorption band
has been correlated with bond dissociation energy,[13] and thus a correlation
for a given metal and metal-metal distance might be expected. Such a
correlation does obtain, but it is curious that the shift to higher energy

in the $\sigma_b \rightarrow \sigma^*$ absorption in the Mo complex is about twice as great as in the W complex. The position of the $\delta_b \rightarrow \delta^*$ absorption in a set of quadruple metal-metal bonded complexes was found to correlate with the M-M distance,[14] and the shift in energy was of the order of 2000 cm^{-1} for a range of M-M distances of ~1.8-2.2Å. Consistent with a shift to higher energy for the M-M absorptions we note that the triple bonded $(\eta^5-C_5H_5)_2M_2(CO)_4$ (M = Mo, W) species themselves do not have a low energy absorption attributable to a $\sigma_b \rightarrow \sigma^*$ transition,[2] and we conclude that such an absorption is at substantially higher energy than for the single bonded $(\eta^5-C_5H_5)_2M_2(CO)_6$. The visible band in the C_2H_2 adducts, as in the parent hexacarbonyls, can be assigned to a $\pi-d \rightarrow \sigma^*$ transition. Thus, we can effectively treat the C_2H_2 adducts as $(\eta^5-C_5H_5)_2M_2(CO)_4L_2$ derivatives of the parent hexacarbonyls with respect to their electronic spectral properties.

These electronic and geometrical structural considerations suggest a rich photochemistry for the C_2H_2 adducts involving metal-metal bond cleavage which is found[12,15-19] in other dinuclear carbonyl complexes exhibiting a low-lying $\sigma_b \rightarrow \sigma^*$ excitation. Preliminary experiments in one of our laboratories (M.S.W.) show the C_2H_2 adducts to be photosensitive, and the work will be published independently.

Acknowledgments

References

1.   (a) Dreyfus Teacher-Scholar Grant Recipient, 1975-1980; (b) NIH
      Research Career Development Awardee, 1975-1980.

2.   (a) D. S. Ginley and M. S. Wrighton, J. Amer. Chem. Soc., 97 (1975) 3533;
      (b) D. S. Ginley, C. R. Bock, and M. S. Wrighton, Inorg. Chim. Acta,
      23 (1977) 85.

3.   R. J. Klingler, W. Butler, and M. D. Curtis, J. Amer. Chem. Soc., 97
      (1975) 3535.

4.   (a) W. I. Bailey, Jr., F. A. Cotton, J. D. Jamerson, and J. R. Kolb,
      J. Organometal. Chem., 121 (1976) C23; (b) W. I. Bailey, D. M.
      Collins, and F. A. Cotton, ibid., 135 (1977) C53.

5.   L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell
      University Press, Ithaca, New York, 1960, Chapter 7.

6.   (a) W. G. Sly, J. Amer. Chem. Soc., 81 (1959) 18; (b) D. A. Brown,
      J. Chem. Phys., 33 (1960) 1037; (c) F. A. Cotton, J. D. Jamerson,
      and B. Stults, J. Amer. Chem. Soc., 98 (1976) 1774.

7.   O. S. Mills and B. W. Shaw, J. Organometal. Chem., 11 (1968) 595.

8.   (a) R. D. Adams, D. M. Collins, and F. A. Cotton, Inorg. Chem., 13
      (1974) 1086; (b) R. D. Adams, D. M. Collins, and F. A. Cotton,
      J. Amer. Chem. Soc., 96 (1974) 749.

9.   J. Potenza, P. Giordano, D. Mastropaolo, and A. Efraty, Inorg. Chem.,
      13 (1974) 2540.

10.   G. G. Sumner, H. P. Klug, and L. E. Alexander, Acta Cryst., 17 (1964) 732.

11.   J. A. Ibers, J. Organometal. Chem., 14 (1968) 423.

12.   M. S. Wrighton and D. S. Ginley, J. Amer. Chem. Soc., 97 (1975) 4246.

13.   J. P. Fawcett, A. J. Poë, and M. V. Twigg, J.C.S. Chem. Comm. (1973) 267.

14.   A. P. Sattelberger and J. P. Fackler, J. Amer. Chem. Soc., 99 (1977) 1258.

15.   (a) M. S. Wrighton and D. S. Ginley, J. Amer. Chem. Soc., 97 (1975)
      2065; (b) D. S. Ginley and M. S. Wrighton, ibid., 97 (1975) 4908;
      (c) D. L. Morse and M. S. Wrighton, ibid., 98 (1976) 3931; (d) H. B.
      Abrahamson and M. S. Wrighton, ibid., 99 (1977) 5510.

16.   R. M. Laine and P. C. Ford, Inorg. Chem., 16 (1977) 388.

17.   C. Giannotti and G. Merle, J. Organometal. Chem., 105 (1976) 97.

18.   (a) J. L. Hughey, C. R. Bock, and T. J. Meyer, J. Amer. Chem. Soc., 97
      (1975) 4440; (b) J. L. Hughey, IV, C. P. Anderson, and T. J. Meyer,
      J. Organometal. Chem., 125 (1977) C49.

19.   B. H. Byers and T. L. Brown, J. Amer. Chem. Soc., 97 (1975) 3270, 947.

Table I Final Positions and Thermal Parameters for $(\eta^5\text{-}C_5H_5)_2W_2(CO)_4(C_2H_2)$ with Estimated Standard Deviations

Atom	x	y	z	B
W(1)	0.24615(9)	0.07797(5)	0.43092(9)	a
W(2)	0.23811(8)	0.24886(5)	0.48778(9)	a
C(1)	0.0715(25)	0.1199(14)	0.3976(27)	3.1(4)
C(2)	0.2275(24)	0.0572(14)	0.6457(28)	3.0(4)
C(3)	0.3957(22)	0.3146(13)	0.4784(24)	2.3(4)
C(4)	0.2234(18)	0.2552(11)	0.2602(21)	1.5(3)
C(5)	0.3890(23)	0.1673(13)	0.4290(24)	2.3(4)
C(6)	0.3649(24)	0.1580(14)	0.5805(26)	2.6(4)
C(7)	0.3161(48)	0.0381(28)	0.1842(52)	7.9(10)
C(8)	0.1925(30)	0.0138(17)	0.1880(32)	4.3(6)
C(9)	0.2990(37)	0.4588(22)	0.1751(42)	6.1(7)
C(10)	0.1790(33)	0.4540(19)	0.1152(37)	5.0(6)
C(11)	0.1112(35)	0.4989(20)	0.1904(36)	5.5(7)
C(12)	0.0308(21)	0.2886(12)	0.5118(23)	2.0(3)
C(13)	0.1086(26)	0.3553(15)	0.5365(28)	3.3(5)
C(14)	0.1967(28)	0.3433(16)	0.6738(32)	4.0(5)
C(15)	0.1643(31)	0.2716(18)	0.7365(35)	4.5(6)
C(16)	0.0629(22)	0.2358(13)	0.6407(25)	2.6(4)
O(1)	0.4585(19)	0.3696(11)	0.8726(21)	4.1(4)
O(2)	0.2107(24)	0.0391(14)	0.7732(28)	6.3(5)
O(3)	0.4793(18)	0.3562(10)	0.4695(19)	3.9(3)
O(4)	0.2142(18)	0.2603(10)	0.1284(21)	3.8(3)

footnote: a) Anisotropic Temperature Factors:

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W(1)	0.00727(11)	0.00136(3)	0.00870(13)	-0.00017(4)	0.00008(8)	-0.00004(5)
W(2)	0.00522(9)	0.00141(3)	0.00746(12)	-0.00000(4)	0.00028(7)	-0.00011(4)

The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

Table II Selected Distances (in Å) and Angles (in degrees) of

$(\eta^5-C_5H_5)_2W_2(CO)_4(C_2H_2)$ (standard deviation in parenthesis)

(A) Interatomic Distances

W(1)-W(2)	2.973(1)	C(5)-C(6)	1.35(3)
W(1)-C(1)	1.93(3)	W(2)-C(3)	1.98(2)
W(1)-C(2)	1.90(2)	W(2)-C(4)	1.95(2)
W(1)-C(5)	2.12(2)	W(2)-C(5)	2.17(2)
W(1)-C(6)	2.18(2)	W(2)-C(6)	2.14(2)
W(1)-C(7)	2.39(4)	W(2)-C(12)	2.26(2)
W(1)-C(8)	2.38(3)	W(2)-C(13)	2.31(3)
W(1)-C(9)	2.27(4)	W(2)-C(14)	2.45(3)
W(1)-C(10)	2.30(3)	W(2)-C(15)	2.35(3)
W(1)-C(11)	2.30(3)	W(2)-C(16)	2.32(2)
W(1)...C(3)	>3.5	W(2)...C(1)	2.86(2)
W(1)...C(4)	3.37(2)	W(2)...C(2)	>3.5
C(1)-O(1)	1.18(3)	C(3)-O(3)	1.12(3)
C(2)-O(2)	1.16(3)	C(4)-O(4)	1.13(3)

(B) Interatomic Angles

Atoms	Angle	Atoms	Angle
C(1)-W(1)-C(2)	92.9(10)	C(3)-W(2)-C(4)	85.8(8)
C(5)-W(1)-C(6)	36.6(8)	C(5)-W(2)-C(6)	36.5(8)
W(1)-C(5)-W(2)	87.6(9)	W(1)-C(6)-W(2)	86.8(9)
W(1)-C(1)-O(1)	166.9(21)	W(2)-C(3)-O(3)	175.0(20)
W(1)-C(2)-O(2)	174.5(22)	W(2)-C(4)-O(4)	178.7(17)
W(2)-W(1)-C(1)	67.7(7)	W(1)-W(2)-C(3)	121.5(6)
W(2)-W(1)-C(2)	91.1(7)	W(1)-W(2)-C(4)	83.8(6)
W(1)-C(1)-W(2)	73.8(8)	W(2)-C(1)-O(1)	119.3(17)

Table III. M-M and C-C Distances in Relevant Molecules.

Species	M-M, Å	C-C, Å	Reference
ethane	--	1.533	5
ethylene	--	1.334	5
acetylene	--	1.204	5
benzene	--	1.397	5
$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$	3.235	--	8
$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$	2.448	--	3
$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_2H_2)$	2.984	--	4b
$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_2Et_2)$	2.977	--	4a
$(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$	3.280	--	8b
$(\eta^5\text{-}C_5(CH_3)_5)_2Cr_2(CO)_4$	2.280	--	9
$(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$	3.222	--	8
$(\eta^5\text{-}C_5H_5)_2W_2(CO)_4(C_2H_2)$	2.973	1.35 (C_2H_2)	This work
$Co_2(CO)_6(C_2Ph_2)$	2.47	1.369 (C_2Ph_2)	6a,b
$Co_2(CO)_6(C_2\underline{t}Bu_2)$	2.463	1.335 ($C_2\underline{t}Bu_2$)	6c
$Co_2(CO)_8$	2.52	--	10
$Co_2(CO)_6(P(n\text{-}Bu)_3)_2$	2.66	--	11
$(\eta^5\text{-}C_5H_5)_2Ni_2(C_2Ph_2)$	2.33	1.35	7
$(\eta^5\text{-}C_5H_5)_2Ni_2(CO)_2$	2.36	--	7

Table IV. Comparison of the Structural Parameters of $(\eta^5-C_5H_5)_2W_2(CO)_4(C_2H_2)$ with Related Molecules
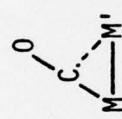
(A) Molecules with a semi-bridging CO group

Compound	M-M	M-C	M'...C	M'-M-C	M-C-O	IR bands(in alkanes)	Reference
$(\eta^5-C_5H_5)_2W_2(CO)_4(C_2H_2)$	2.973(1)	1.93(3)	2.86(2)	67.7(7)°	167(2)°	1990, 1922, 1835cm⁻¹	this work
$(\eta^5-C_5H_5)_2Mo_2(CO)_4(C_2H_2)$	2.984(1)	-	2.911(4)	-	-	1990, 1930, 1840cm⁻¹	4b
$(\eta^5-C_5H_5)_2Mo_2(CO)_4(C_2Et_2)$	2.977(1)	1.936(6)	2.826(6)	66.3°	-	1997, 1930, 1852cm⁻¹	4a

(B) Molecules with a metal-metal triple bond

Compound	M-M	M-C	M'...C	M'-M-C	M-C-O	IR bands(in alkanes)	Reference
$(\eta^5-C_5H_5)_2Mo_2(CO)_4$	2.448(1)	2.13(5)	2.55(5)	67(1)°	176(1)°	1889, 1859cm⁻¹	3
$(\eta^5-C_5Me_5)_2Cr_2(CO)_4$	2.280(2)	1.842(6)	2.474(5)	73.0(3)°	170.8(6)°	1876, 1857cm⁻¹	9
		1.822(6)	2.633(5)	79.1(3)°	174.8(6)°		

Table V. Absorption Maxima and M-M Distance in $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ and $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4(C_2H_4)$.[a]

Complex	M-M, Å	$\sigma\rightarrow\sigma^*$, cm^{-1} ($\varepsilon$)	$\pi\text{-}d\rightarrow\sigma^*$, cm^{-1} ($\varepsilon$)
$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$	3.235[b]	25,640 (23,200)	19,530 (2300)
$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_2H_4)$	2.984[c]	27,700 (7400)	18,760 (850)
$(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$	3.222[b]	27,590 (21,000)	20,410 (2850)
$(\eta^5\text{-}C_5H_5)_2W_2(CO)_4(C_2H_4)$	2.973	28,370 (6000)	19,050 (900)

[a]All spectral data are for 298°K C_6H_6 solutions recorded using a Cary 17 uv-vis-nir spectrophotometer.

[b]Ref. 8.

[c]Ref. 4b.

Captions for the figures:

Figure 1:   The Molecular Geometry of $(\eta^5-C_5H_5)_2W_2(CO)_4(C_2H_2)$

Figure 2:   Electronic spectra in EPA solution at 298°K (——) and upon cooling
            to 77°K (---). Spectral changes upon cooling are not corrected
            for solvent contraction. Band maxima and absorptivities in C_6H_6
            at 298°K are given in Table V.

Figure 3:   Electronic spectra in EPA solution at 298°K (——) and upon cooling
            to 77°K (---). Spectral changes upon cooling are not corrected
            for solvent contraction. Band maxima and absorptivities in C_6H_6
            at 298°K are given in Table V.

Figure 4:   Electronic spectra in EPA solution at 298°K (——) and upon cooling
            to 77°K (---). Spectral changes upon cooling are not corrected
            for solvent contraction. Band maxima and absorptivities in
 C_6H_6 at 298°K are given in Table V.

Figure 1

$(\eta^5 - C_5H_5)_2Mo_2(CO)_4(C_2H_2)$
in EPA ——— 298°K
- - - - 77°K

$(\eta^5 - C_5H_5)_2W_2(CO)_4(C_2H_2)$
in EPA ——— 298°K
- - - - 77°K